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Haiduke, R.L.A.; Silva, A.M.; Visscher, L.

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The nuclear electric quadrupole moment of antimony from the molecular method

Roberto L. A. Haiduke and Albérico B. F. da Silva

Departamento de Química e Física Molecular, Instituto de Química de São Carlos, C.P. 780, São Carlos, São Paulo 13560-970, Brazil

Lucas Visscher^{a)}

Department of Theoretical Chemistry, Faculty of Sciences, Vrije Universiteit Amsterdam, De Boelelaan 1083 HV Amsterdam, Netherlands

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Relativistic Dirac-Coulomb (DC) Hartree-Fock calculations are employed to obtain the analytic electric field gradient (EFG) on the antimony nucleus in the SbN, SbP, SbF, and SbCl molecules. The electronic correlation contribution to the EFGs is included with the DC-CCSD(T) and DC-CCSD-T approaches, also in the four-component framework, using a finite-difference method. The total EFG results, along with the experimental nuclear quadrupole coupling constants from microwave spectroscopy, allow to derive the nuclear quadrupole moments of ¹²¹Sb and ¹²³Sb, respectively, as −543(11) and −692(14) mb. © 2006 American Institute of Physics.
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I. INTRODUCTION

The molecular method for the obtention of nuclear quadrupole moments (NQMs) has become a popular way of determining these quantities in recent studies, as demonstrated by the “year-2001” compilation of NQMs.¹ This method is based on the calculation of electric field gradient (EFG) values for a certain number of molecules that are further combined with experimental nuclear quadrupole coupling constants (NQCCs), obtained from microwave spectroscopy, to yield the NQMs for the desired nucleus. High accuracy can be achieved for the NQMs derived in such a way depending on the quality of the EFG calculations and the errors of experimental NQCCs. In the context of the available NQM values, the antimony nucleus presents the greatest proportional uncertainties among the stable main group elements,^{1,2} what was attributed to the lack of high quality NQCC values for a range of molecules containing this atom. Fortunately, the recent determination of accurate NQCCs for SbN, SbP, SbF, and SbCl (Ref. 2 and 3) makes possible the use of the molecular method to attain a more reliable value for the Sb NQMs.

The NQM, $Q(X)$, of the X atom in a linear molecule (in barns) is given by

$$Q(X) = \frac{\nu_Q(X)}{234.9647q(X)}, \quad (1)$$

where $\nu_Q(X)$ and $q(X)$ are, respectively, the NQCC and the EFG of this atom.

The derivation of NQMs for heavy atoms by the molecular method is still a challenge since the accuracy of EFG calculations in such systems requires accurate treatment for both relativistic and electronic correlation contributions.^{4,5}

One of the most precise ways of dealing with relativistic effects is given by the four-component Dirac-Coulomb (DC) approach. The electronic correlation, except in systems with uncommon electronic structures, can be well described with a coupled cluster method in which a cluster operator containing only single and double excitations (CCSD) is corrected for triple contributions in a noniterative way, either using the CCSD(T) (Ref. 6) or the more recent CCSD-T (Ref. 7) formulation. Finally, in order to attain high quality EFG results, an accurate relativistic basis set is required. As a good description of the core region is essential in EFG calculations, a number of additional tight functions needs to be added to standard sets to reach the required accuracy in the computed EFG values.^{4,5}

In this work, the chosen antimony basis set is the relativistic adapted Gaussian basis set (RAGBS) (Ref. 8) that presents an error of only 1 mhartree with respect to the numerical reference values and is designed to furnish a precise description of the innermost region. The convergence of the EFG values on the basis set size of antimony is first analyzed by means of DC Hartree-Fock (HF) and density functional DC-B3LYP calculations, in which the number of diffuse and polarization functions is varied. The EFGs for the SbN, SbP, SbF, and SbCl molecules are calculated analytically in the DC-HF method whereas electronic correlation contributions at the DC-CCSD(T) and DC-CCSD-T levels are computed with the finite-difference method. These resulting EFG values are employed in the molecular method to obtain NQMs for antimony.

II. COMPUTATIONAL DETAILS

The calculations in this work were performed with the relativistic four-component DC Hamiltonian. The light speed value adopted in these calculations is 137.035 999 8 a.u. The Gaussian finite nuclear model was chosen,⁹ as it is a better

^{a)}Electronic mail: visscher@chem.vu.nl

TABLE I. Convergence tests for the Sb EFGs and total energies with the Sb basis set on the addition of f and g polarization functions.

Basis set	DC-HF				DC-B3LYP			
	$q(\text{Sb})$	$q(\text{N})$	$\Delta q(\text{Sb})^a$	Energy	$q(\text{Sb})$	$q(\text{N})$	$\Delta q(\text{Sb})^a$	Energy
26s21p16d	-5.194	-1.119		-6535.127 47	-5.480	-0.877		-6538.550 80
+1f	-5.198	-1.116	-0.004	-6535.127 64	-5.478	-0.873	0.002	-6538.551 07
+2f	-5.217	-1.117	-0.020	-6535.128 29	-5.488	-0.872	-0.011	-6538.551 39
+3f	-5.281	-1.121	-0.063	-6535.130 88	-5.541	-0.875	-0.052	-6538.553 15
+4f	-5.289	-1.126	-0.008	-6535.132 29	-5.540	-0.880	0.001	-6538.554 37
+5f	-5.260	-1.127	0.029	-6535.132 73	-5.514	-0.880	0.026	-6538.554 83
+6f	-5.241	-1.127	0.019	-6535.133 07	-5.500	-0.881	0.013	-6538.555 14
+7f	-5.236	-1.128	0.005	-6535.133 20	-5.495	-0.881	0.006	-6538.555 28
+8f	-5.237	-1.128	-0.001	-6535.133 26	-5.497	-0.881	-0.002	-6538.555 35
+9f	-5.237	-1.128	-0.001	-6535.133 27	-5.497	-0.881	0.000	-6538.555 36
26s21p16d6f	-5.233	-1.130		-6535.133 07	-5.495	-0.884		-6538.555 07
+1g	-5.232	-1.129	0.001	-6535.133 08	-5.495	-0.884	0.001	-6538.555 08
+2g	-5.243	-1.128	-0.011	-6535.133 45	-5.501	-0.882	-0.006	-6538.555 31
+3g	-5.253	-1.126	-0.010	-6535.133 74	-5.505	-0.880	-0.005	-6538.555 51
+4g	-5.247	-1.125	0.005	-6535.133 78	-5.498	-0.879	0.007	-6538.555 55
+5g	-5.245	-1.125	0.002	-6535.133 79	-5.497	-0.879	0.002	-6538.555 56

^a $\Delta q(\text{Sb})$ stands for the difference of EFG values between the augmented and previous calculations.

model for the nuclear charge distribution than the more conventional point charge model. To reduce computational cost we neglected small component integral contributions.¹⁰ The calculations were carried out at the experimental equilibrium bond distances of 1.8357, 2.2054, 1.9177, and 2.3355 Å, respectively, for SbN, SbP, SbF, and SbCl.^{2,3,11}

As strong dependencies of the EFG values on the contraction length of the p -function space have been noticed before,^{12,13} the basis sets in our calculations were kept uncontracted. The nonrelativistic cc-pVTZ basis sets of Dunning, Jr.^{14,15} were selected for the N, F, P, and Cl atoms, while the basis set for antimony is the RAGBS.⁸ The basis set sizes are 10s5p2d1f (N and F), 15s9p2d1f (P and Cl), and 25s21p13d (Sb).

For the closed-shell SbN and SbP molecules, we employed the single reference CCSD(T) and CCSD-T methods.¹⁶ The SbF and SbCl molecules are open-shell systems with triplet spin multiplicity. To deal with such systems we employed the Fock-space coupled cluster (FSCC) method¹⁷ that starts with the definition of closed-shell reference systems (SbF⁺ and SbCl⁺) with a subsequent calculation of double electron affinities to end up with the SbF and SbCl results. The perturbative triple corrections were in this case taken from the closed-shell reference system, i.e., the effective Hamiltonian used to determine the correlated electron affinities was determined on basis of a CCSD wave operator. All the calculations were done using the DIRAC 04.1 package.¹⁸

III. RESULTS AND DISCUSSION

A. Complementation of the antimony basis set

The initial step of this work was a basis set convergence study of the antimony EFG value in a selected molecule of the set, SbN, by using the DC-HF and DC-B3LYP methods. This was required to provide a complement to the Sb basis

set that was derived in atomic DC-HF calculations and does not contain the polarization functions needed in a molecular environment. We decided to add to the Sb basis set any function that is able to cause an absolute variation in the Sb EFG value larger than 0.005 a.u. in any of the two approaches chosen, DC-HF and DC-B3LYP.

First, the importance of including additional tight or diffuse s , p , and d functions in the Sb basis set was verified by adding such functions in an independent way, that is, searching for convergence in each case separately. These tight and diffuse functions were generated by the same polynomial expansion used to develop the Sb RAGBS.⁸ This study showed that one tight d (12 547.99), one diffuse s (0.029 200 27), and two diffuse d (0.107 449 8 and 0.037 116 75) functions are sufficient to achieve the desired Sb EFG accuracy (the values in parentheses are the function exponents).

We then determined the polarization functions that should be added to the new 26s21p16d set. For efficiency reasons, the Sb polarization f and g functions were, respectively, selected as subsets of the p - and d -function space. Polarization f functions were added one after another, starting with the small exponents and proceeding to tighter functions of the p -function space, until convergence of the Sb EFG value was reached. In Table I, the results for the convergence test with polarization functions are presented. Six polarization f functions (6.141 739, 3.161 871, 1.579 023, 0.755 128 7, 0.341 380 4, and 0.144 025 1) proved to be needed to reach the demanded accuracy, from the second to the seventh function in Table I. Using now this 26s21p16d6f set, the same procedure was carried out for the polarization g space which showed that three g functions should be considered (1.395 558, 0.645 779 7, and 0.276 571 2), from the second to fourth function in Table I. As expected, both calculation approaches (DC-HF and DC-B3LYP) indicate that, in general, the same functions are important. This choice was

also supported by the analysis of the orbital contributions that provide a more detailed picture of the convergence process. Moreover, also the total electronic energy follows a similar convergence pattern to that of the EFGs, with functions leading to large lowering of the total energies being also important to the Sb EFG description. Hence, the final basis set size for antimony is defined as 26s21p16d6f3g. This basis set was used to obtain all of the analytic EFG results at the DC-HF and density functional, DC-B3LYP and DC-BPW91, approaches.

B. The finite-difference method and the active space choice

The DC-CCSD(T) and DC-CCSD-T correlation contributions to the EFG were obtained with the finite-difference method. This method, in a two-point form, is given by

$$\left(\frac{\partial E(\lambda)}{\partial \lambda}\right)_0 \approx \frac{E(+\lambda) - E(-\lambda)}{2\lambda}, \quad (2)$$

where E can be the total energy or just the electronic correlation energy and λ is the applied field strength.

The finite-difference method has a major limitation in the finite-field strength value that can be used. This strength should be small enough to remain in the linear response regime, while at the same time it should be large enough to prevent numerical inaccuracies due to incomplete convergence of iterative procedures and other sources of numerical noise. Based on a series of tests, we decided to employ an absolute field strength value of 1×10^{-7} a.u.. Among these tests, the EFG contributions at the Sb nucleus obtained from analytic second-order Moller-Plesset (DC-MP2) calculations with SbN and SbP are compared with finite-difference results (by using the DC-MP2 correlation energies) and the agreement observed between both approaches was excellent.

The presence of p functions with large exponents (roughly about 10^7) is of particular importance as any small inaccuracy in the core spinor coefficients associated with these tight p functions (core $p_{1/2}$ and $p_{3/2}$ atomiclike orbitals) can be responsible for large deviations in the obtained EFGs. This is easily seen by considering the contribution from a particular p -type basis function χ_q to the EFG,

$$\Delta q_{zz} = \sum_i |c_{q,i}^x|^2 \langle \chi_q^x | \hat{q}_{zz} | \chi_q^x \rangle + |c_{q,i}^y|^2 \langle \chi_q^y | \hat{q}_{zz} | \chi_q^y \rangle + |c_{q,i}^z|^2 \langle \chi_q^z | \hat{q}_{zz} | \chi_q^z \rangle. \quad (3)$$

If the density of a p shell is spherical, this contribution is zero since

$$\langle \chi_q^x | \hat{q}_{zz} | \chi_q^x \rangle = \langle \chi_q^y | \hat{q}_{zz} | \chi_q^y \rangle = -\frac{1}{2} \langle \chi_q^z | \hat{q}_{zz} | \chi_q^z \rangle, \quad (4)$$

and the sums of squares of MO coefficients $c_{q,i}$ are equal,

$$\sum_i |c_{q,i}^x|^2 = \sum_i |c_{q,i}^y|^2 = \sum_i |c_{q,i}^z|^2. \quad (5)$$

In molecules one will see small deviations from zero due to the polarization that changes the occupation of the x , y , and z components of the basis functions. This effect is small for the tightest p functions, but due to the scaling of the EFG matrix element,

$$\langle \chi_q^z | \hat{q}_{zz} | \chi_q^z \rangle = -\frac{8}{15\sqrt{\pi}} (2\alpha_p)^{3/2}, \quad (6)$$

with the size of the exponent α_p one needs to achieve high precision in the molecular orbital coefficients of these exponents.

The problem with the finite-field method lies in the fact that high exponents create large perturbations even with rather modest field strengths. With a field strength of 1×10^{-7} , the tightest Sb p functions (3 767 144 and 766 046.1) give rise to matrix elements of -627 and -57 a.u., respectively, which are too large to be considered as small perturbations. This forced us to delete these two Sb tight p functions in order to reach stable finite-difference results (checked by the comparison of the analytic and the finite-difference results of DC-HF calculations). Fortunately, the absence of these tight p functions resulted in only a negligible variation of the DC-HF analytic EFG values, indicating that they do not contribute significantly to the EFG.

Finally, by similar arguments concerning the iterative solution of the CCSD equations, the active space for the DC-CCSD(T) and DC-CCSD-T calculations was restricted to exclude the core $4p_{1/2}$ and $4p_{3/2}$ atomiclike orbitals since their inclusion made the finite-difference electronic correlation contributions unstable. The active space was then defined to be in an energy range between -3 and 20 a.u. Of course, the subvalence core orbitals for N, F, P, and Cl are also excluded from the active space with this energy range. On the other hand, the maintaining of the core Sb $4d$ orbitals in the active space is supported by an energetic splitting of roughly 3 hartree between such orbitals and the $4p$ ones. After the reduction of the active space, the DC-CCSD(T) and DC-CCSD-T correlation contributions to the Sb EFGs showed a linear behavior, in a similar way to a previous work that focused on ^{27}Al and ^{69}Ga atoms,¹⁹ and the simple two-point approach of Eq. (2) was adequate to estimate these contributions to the EFGs. The same previous study also noticed the difficulty in defining the active space when using the finite-difference method.¹⁹

The care that must be dispensed to the p -function space is a direct consequence of the huge and almost mutually canceling contributions from the core p orbitals, as can be clearly noticed in Fig. 1 (that presents the orbital decomposition of the Sb EFG value in SbN), as given by the DC-HF analytic calculation. Hence, the total electronic part of the EFGs is simply a sum of these orbital contributions. As one can see, the largest absolute values in Fig. 1(a) are those from the core $2p_{3/2}$ atomiclike orbitals (roughly 3670 a.u.). The core $4p_{3/2}$ orbitals are those numbered as 18 and 19 in Fig. 1(b) and are also associated with large contributions to the Sb EFG (122 and -126 a.u.). The most diffuse region, beyond the core Sb $4p$ orbitals, is responsible for roughly 80% of the total electronic part of the Sb EFG, as given by the analytic DC-HF calculation. Moreover, in this region the contributions are not canceled mutually, indicating the large polarization of the valence electronic cloud.

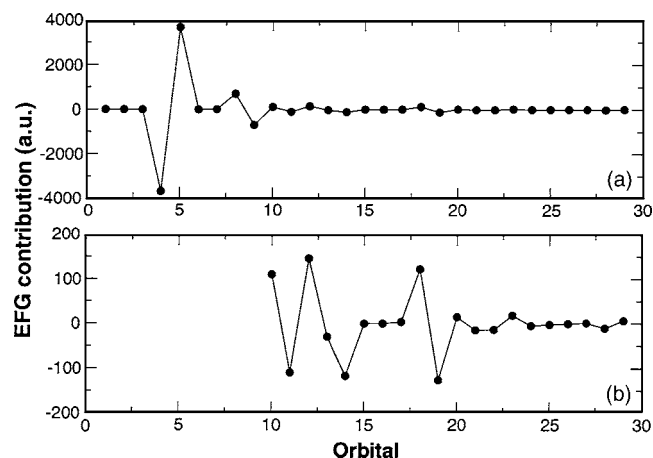


FIG. 1. (a) DC-HF orbital contributions to the total electronic part of the Sb EFG in SbN. (b) Detail of the region beyond Orbital No. 9 (core Sb $3p_{3/2}$).

C. The nuclear quadrupole moment of antimony

Table II shows the EFG values for SbN, SbP, SbF, and SbCl obtained in this work. These quantities are employed in conjunction with the experimental NQCCs (Refs. 2 and 3) to yield the NQMs, as seen in Table III, for the two stable antimony isotopes (^{121}Sb and ^{123}Sb). Each method, for both isotopes, presents an agreement for NQMs from the results involving only closed shell (last two columns in Table III) and those obtained with all molecules (see also Table III) within the range given by the mean absolute deviations (MADs). However, it is clear in Table III that the results for the open-shell molecules, SbF and SbCl, exhibit large deviations, in particular, with the DC-CCSD approach. One can also notice that the DC-CCSD(T) and DC-CCSD-T NQM values show a considerable difference in the case of SbN and SbCl (more than 20 mb). The smallest MADs are those obtained with our best theoretical approach, DC-CCSD-T, that is more complete in including the fourth- and fifth-order interactions than the DC-CCSD(T).⁷

Considering only the NQM results for SbN and SbP, Table III shows that DC-B3LYP and DC-BPW91 values are in close agreement to the DC-CCSD ones. Moreover, there is a clear decrease tendency in the average NQMs in these

TABLE II. EFGs at the antimony nucleus (in atomic units) for the SbN, SbP, SbF, and SbCl molecules. The analytic results (indicated by asterisks) were obtained with the $26s21p16d6f3g$ basis set for the Sb atom while the finite-difference ones were calculated using a $26s19p16d6f3g$ basis set (as discussed in the text).

Method	SbN	SbP	SbF	SbCl
DC-HF*	-5.245	-6.174	4.388 ^a	3.784 ^a
DC-B3LYP*	-5.497	-5.146	^b	^b
DC-BPW91*	-5.421	-4.947	^b	^b
DC-CCSD	-5.299	-5.162	3.971	3.100
DC-CCSD(T)	-4.918	-4.881	4.571	4.338
DC-CCSD-T	-5.097	-4.860	4.461	4.150

^aDC-HF values obtained from average of configuration calculations.

^bThese values could not be calculated with DIRAC 04.1.

systems going from the DC-HF (-477.4 mb in ^{121}Sb) to DC-CCSD (-516.6 mb in ^{121}Sb) and finishing with the inclusion of triple contributions [-551.5 and -542.8 mb, respectively, for DC-CCSD(T) and DC-CCSD-T in ^{121}Sb]. Hence, the electronic correlation tends to reduce the antimony NQM in these closed-shell systems. The rather large disagreement between the NQMs for antimony obtained with the EFGs calculated for SbN by using the DC-CCSD(T) and DC-CCSD-T methods could be caused by a large value of a single excitation amplitude that shows up in a fifth-order perturbation term [see first term of Eq. (14) in Ref. 7]. As this higher-order correction is lacking in MP2 this may also be the reason that the DC-MP2 analytic and finite-difference results (not shown here) are completely different from the ones given by coupled cluster and density functional approaches.

The MADs are obtained by using only the deviations in the estimated NQMs, that include the errors in the experimental NQCCs. The basis set error in the EFG calculations is expected to be negligible given the convergence analysis carried out here, in which a 0.005 a.u. threshold (less than 0.1%) was reached. The Gaunt (G) integrals, not considered here, may probably introduce an error of less than 0.2% for antimony, under comparison with EFG results for other atoms with similar number of electrons⁵ and as estimated by

TABLE III. NQMs for ^{121}Sb and ^{123}Sb (in mb) obtained with the EFGs and NQCCs for the SbN, SbP, SbF, and SbCl molecules. The analytic results (indicated by asterisks) were obtained with the $26s21p16d6f3g$ basis set for the Sb atom while the finite-difference ones were calculated using a $26s19p16d6f3g$ basis set (as discussed in the text).

Isotope	Method	SbN	SbP	SbF	SbCl	Average	MAD	Average ^a	MAD ^a
^{121}Sb	DC-HF*	-527.2	-427.6	-569.1	-579.4	-525.8	49.1	-477.4	49.8
	DC-B3LYP*	-503.0	-513.0	^b	^b	-508.0	5.0
	DC-BPW91*	-510.0	-533.7	^b	^b	-521.8	11.8
	DC-CCSD	-521.8	-511.4	-628.9	-707.3	-592.4	75.7	-516.6	5.2
	DC-CCSD(T)	-562.2	-540.9	-546.4	-505.3	-538.7	16.7	-551.5	10.6
	DC-CCSD-T	-542.5	-543.2	-559.8	-528.3	-543.4	8.2	-542.8	0.4
	Reference 20							-360(40)	
^{123}Sb	Reference 21							-669(15)	
	Reference 22							-530(100)	

^aThese averages and mean absolute deviation (MADs) were calculated using only the SbN and SbP results.

^bThe EFG values could not be calculated with DIRAC 04.1.

DCG-HF calculations in SbN and SbP molecules. However, a larger error is to be expected considering other remaining deficiencies in the EFG calculations, mainly the underestimation of core correlation, high-lying virtual spinors, and higher-order electronic correlation effects. The latter one is assumed here in an upper limit as 1%.⁴ Core correlation and high-lying virtual spinors may roughly introduce an error of up to 0.8% as was verified by performing a few additional finite-difference MP2 calculations that do not suffer of the active space problems encountered in the iterative solution of the DC-CCSD equations (mentioned in Sec. III B). In summary, we will assume a total error of 2.0% in our EFG calculations.

IV. CONCLUSIONS

The recommended NQM values for ¹²¹Sb and ¹²³Sb, reached with DC-CCSD-T EFG values, are given, respectively, as −543(11) and −692(14) mb. The DC-CCSD-T approach performed surprisingly well, clearly better than the more commonly used DC-CCSD(T) treatment of triple excitations. The NQMs of this work are in disagreement with the ones presented in the “year-2001” compilation of NQMs (Ref. 1) obtained by the atomic method that are −360(40) and −490(50).²⁰ The most recent NQMs, determined by Svane²¹ using solid state EFG calculations, are −669 and −853 mb. Actually, Svane’s results²¹ are also far away from our results but exhibit the same ratio $q(^{123}\text{Sb})/q(^{121}\text{Sb})$, indicating that the two different experimental sources of NQCC are in agreement and the error is due to the theoretical treatment. An astonishing agreement is observed with the older NQMs values of Murakawa,²² who obtained −530(100) and −680(100) mb in 1955 by studying the hyperfine structure of atomic spectra. This suggests that the currently accepted year-2001 NQM values are wrong and should be replaced by our new values.

The low accuracy of the EFGs calculated for open-shell molecules could be caused by insufficient electronic correlation of the double electron affinities and by a poor description of the DC-HF orbitals used in the Fock-space coupled cluster method, since that orbitals are obtained for the SbF⁺2 and SbCl⁺2 systems. The DC-FSCSD-T method appears to perform reasonably well in these cases, with average values for the NQMs, for ¹²¹Sb and ¹²³Sb, of −543.4 and

−692.8 mb, respectively, which have a good agreement with the values obtained for the closed-shell molecules.

Note added in proof: An independent determination of the nuclear quadrupole moment via the molecular method was published very recently by Demovic *et al.*, J. Chem. Phys. **124**, 184308 (2006). Their recommended value for the nuclear quadrupole moment of ¹²¹Sb is −556(24) mb, in satisfactory agreement with our value.

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